Indian J. Phys. **75A** (4), 307-312 (2001)

IJP A
— an international journal

Hopping conduction in vanadium and iron tellurite glasses

H Sakata

Department of Applied Chemistry, Tokai University,
1117, Kitakaname, Hiratsuka, Kanagawa 259-1292, Japan

E-mail : skt@keydpi cc.u-tokai.ac.jp

Abstract : Dc transport properties of vanadium and iron tellurite glasses are reviewed Glasses of both systems exhibit small polaron hopping conduction Vanadium tellurite glasses indicate adiabatic and non-adiabatic small polaron hopping conduction, while iron tellurite glasses present only non-adiabatic small polaron hopping transport due to lower concentration of maximum Fe_2O_3 content for glass forming. The former produces variable-range hopping conduction depending on glass composition at temperatures lower than $\Theta_D / 4$, but the latter provides no variable-range hopping transport in the measurable range of temperatures The application of pressure on some glasses of both systems increases conductivity Oxygen gas-sensing behaviour due to gas diffusion are found for both kinds of the glasses

Keywords . Small polaron hopping conduction, vanadium and iron tellurite glasses, pressure effect, gas-sensing

PACS Nos. 72 20 -i, 71 38.-k, 81 05.Kf

1. Introduction

Semiconducting properties of oxide glasses containing transition metal ions have attracted interests of researchers and, hence, a number of studies were carried out for clarifying their conduction mechanism. Above all vanadium phosphate [1-4] and borate [5] glasses were investigated. Iron phosphate, silicate, and borate semiconducting glasses then became target for study [6] The conduction of vanadate and iron oxide glasses was generally understood [6,7] by the Mott-Austin's small polaron hopping (SPH) model [8].

Kozhukharov *et al.* [9] found the first binary tellurite glass forming systems containing different transition metal oxides. Semiconducting tellurite glasses then began to investigate [10] and attempts aiming at electronic memory application were also reported [11, 12]. The present report briefly reviews results obtained from recent studies on vanadium and iron tellurite glasses focused on dc conduction properties and their application.

2. Structure

From IR studies carried out earlier, TeO_2 in tellurite glasses was revealed to have trigonal pyramidal TeO_3 or tetragonal pyramidal TeO_4 [13, 14] structural unit. Thus TeO_2 network former makes TeO_3 and/or TeO_4 polyhedra in tellurite glasses. V_2O_5, on the other hand, is known to form VO_5 [15, 16] structural unit. VO_5 pyramids are linked together in glasses containing V_2O_5 [17]. In contrast, iron oxide is not a conventional glass network former. Iron oxide in V_2O_5–MoO_3–Fe_2O_3 glasses [18] is incorporated as FeO_4 tetrahedra and FeO_6 octahedra besides VO_5 groups. In Fe_2O_3–PbO–SiO_2 glasses [19], however, Fe ion builds ordered microclusters with various numbers of Fe ions and makes tree-like configurations [19]. Accordingly, TeO_2 network in tellurite glasses can incorporate VO_5, FeO_4 or FeO_6 structural units, together with other ions, in certain compositional ranges of binary or ternary glasses. From the glass formation study of binary tellurite glasses [9], upper limits for V_2O_5 and Fe_2O_3 were found to be 58 mol% and 20 mol%, respectively, which influenced on electrical transport properties of these glasses.

3. DC conduction

3.1. Small polaron hopping conduction :

As is well known, Austin and Mott [8] proposed a SPH model based on single optical phonon under strong electron-phonon interaction. In this SPH model, the dc conductivity (σ) of a glass with single transition metal ion in non-adiabatic approximation is given by [8],

$$\sigma = \nu_0 N e^2 R^2 C(1-C) \exp(-2\alpha R) \exp(-W / kT) / kT, \quad (1)$$

$$W = W_H + W_D / 2 \quad (T > \Theta_D / 2), \quad (2a)$$

$$W = W_H \quad (T < \Theta_D / 4), \quad (2b)$$

where v_0 is the optical phonon frequency ; N, the density of transition metal ion; R, the mean spacing between transition metal ions ; C, the fraction of reduced transition metal ion ; α, the tunneling factor ; W, the activation energy; W_H, the hopping energy; W_D, the disorder energy and e, T, k, Θ_D have usual definitions, respectively. Almost all electronic conducting oxide glasses containing transition metal ions have been treated by this SPH model which explained well their *dc* conductivity.

For temperatures below $\Theta_D / 4$, normally 100K, where polaron binding energy becomes smaller, the Mott variable-range hopping conduction (VRH) [20] given by

$$\sigma = B\exp(-A / T^{1/4}), \tag{3}$$

$$A = 2.06\,[\alpha^3 / kN(E_F)]^{1/4} \tag{4}$$

is possible to occur, where α is the tunneling factor and $N(E_F)$, the state density at the Fermi level, k, the Boltzmann constant and B, a constant for the temperature range of VRH.

The *dc* conductivity of V_2O_5–TeO_2 glasses studied by Dhawan *et al.* [10] indicated that the conductivity was slightly higher than that of vanadium phosphate glasses, and small polaronic hopping was confirmed. These glasses [10] also presented a $\sigma \propto T^{-1/4}$ behaviour due to VRH [20] [eq. (3)]. On the other hand, V_2O_5–Sb_2O_3–TeO_2 glasses [21], n-type semiconducting, exhibited the linearity between log (σT) and T^{-1} for different glass compositions as shown in Figure 1, which was confirmed to be SPH conduction but no VRH transport was

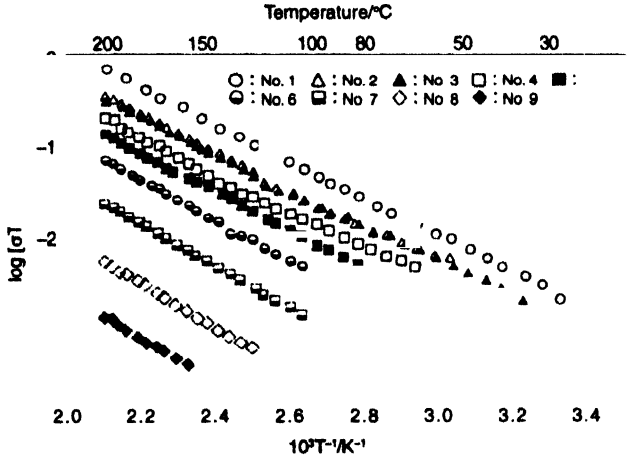

Figure 1. Temperature dependence of dc conductivity for V_2O_5–Sb_2O_3–TeO_2 glasses [21]. The glass composition for each sample is listed in Ref. [21].

observed at low temperatures. V_2O_5–SnO–TeO_2 glasses [22] which were n-type semiconducting but had a p-type semiconducting composition, gave SPH transport with high conductivity, and exhibited the $\sigma \propto T^{-1/4}$ relationship characterizing VRH from 200K to room-temperature [23] (Figure 2). The difference in the occurrence of VRH between two kinds of vanadium tellurite glasses is probably due to differences of $N(E_F)$.

The transition from non-adiabatic to adiabatic transport in SPH occurred normally at about a 50 mol% V_2O_5 for vanadium terullite glasses [21, 22] ; SPH became adiabatic for V_2O_5 content

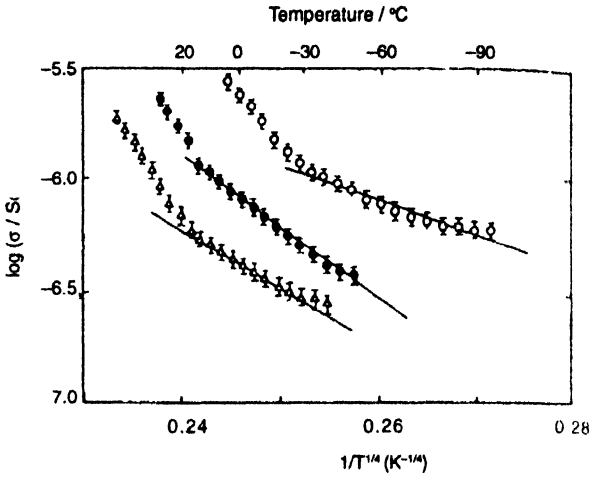

Figure 2. log σ *vs* $T^{1/4}$ for V_2O_5–SnO–TeO_2 glasses [23]. ○ : V_2O_5:SnO:TeO_2 = 50:20:30 ; ● : V_2O_5:SnO:TeO_2 = 50:10:40 ; Δ · V_2O_5:SnO:TeO_2 = 40:10:50 (mol%)

larger than about 50mol%, and non-adiabatic, smaller than this value. This value was similar to other vanadium phosphate glasses [4]. V_2O_5-PbO glasses [24], however, were exceptional since these glasses indicated non-adiabatic SPH at high temperatures for high contents (60–90 mol%) of V_2O_5. The maximum V_2O_5 content for ternary vanadium tellurite glasses was as large as 70mol% [21, 22], so these glasses normally contained both adiabatic and non-adiabatic hopping conduction regions.

The effect of the second transition metal ion on vanadium or iron tellurite glasses was reported for ternary glass forming systems but results were various. The conductivity of Fe_2O_3–V_2O_5–TeO_2 glasses [25] was larger for Fe_2O_3 = 10 and 15 mol% than that for Fe_2O_3 = 5 mol% for V_2O_5 = 50 mol%. V_2O_5–MnO–TeO_2 glasses [26], however, conductivity decreased with increase in MnO for V_2O_5 = 60 mol%. Fe_2O_3–MoO_3–TeO_2 glasses [27], by contrast, the conductivity increased by adding of MoO_3 for fixed Fe_2O_3 content. To analyze these, extension of SPH theory for the glasses containing two transition metal ions is expected.

As eq. (1) shows the conductivity σ is highly influenced by the fraction of reduced transition metal ion (C). The value of C is varied by the amount of transition metal oxide. For V_2O_5–Sb_2O_3–TeO_2 glasses [21] $C(= C_V = [V^{4+}]/\{[V^{4+}]+[V^5]\})$ value decreased with increasing V_2O_5 content ; the results were explained by the effect of a redox reaction $2V_2O_5 + SB_2O_3 \rightarrow 4VO_4 + Sb_2O_5$. A similar decrease in Cv was found for V_2O_5–SnO–TeO_2 glasses [22] for increasing V_2O_5 with fixed SnO contents (Figure 3a) because of a redox reaction $V_2O_5 + SnO \rightarrow 2VO_2 + SnO_2$, and the conductivity lowered with increasing Cv value (Figure 3b) irrespective of a decrease in activation energy

(Figure 3a). For ternary iron tellurite glasses, however, opposite cases were found. Fe_2O_3–Sb_2O_3–TeO_2 [28] and Fe_2O_3–SrO–TeO_2 [29] glasses gave $C(= C_{Fe} = [Fe^{2+}]/\{[Fe^{2+}]+[Fe^{3+}]\})$

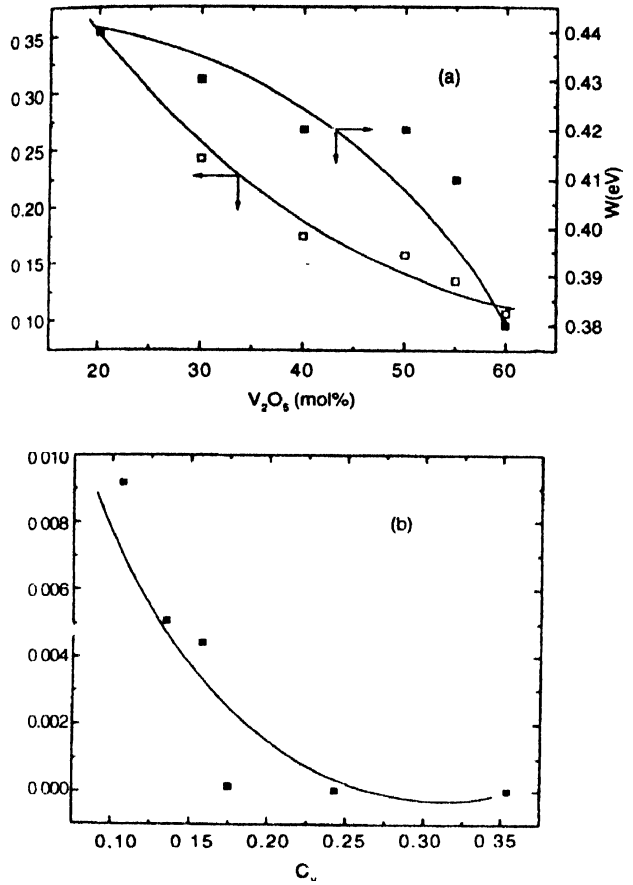

Figure 3. Effects of V_2O_5 content on Cv and activation energy W for V_2O_5 - SnO - TeO_2 glasses [22] (a) Cv and W *vs* V_2O_5 content, (b) Conductivity *vs* Cv

values increased with increasing Fe_2O_3 content (Figure 4a [30]), where the conductivity increased proportionally with increasing C_{Fe} (Figure 4b [30]). This was due to a decrease in activation energy with increasing Fe_2O_3 concentration [28, 29]. Thus C value does not decisively determine the value of conductivity σ of these tellurite glasses, because the conductivity is also related to activation energy as shown in eq. (1).

The conductivity of iron-tellurite glasses was generally high σ values for Fe_2O_3–TeO_2 glasses [31] were a factor of 10^4 larger than that of P_2O_5–Fe_2O_3–CaO glasses [32]. Other ternary iron tellurite glasses, *e.g.*, Fe_2O_3–Sb_2O_3–TeO_2 [28] or Fe_2O_3–SrO–TeO_2 [29] glasses also gave $\sigma = 10^{-5} - 10^{-6}$ Scm^{-1} (Figure 4b) [30] with linearities between log (σ T) and T^{-1} (Figure 5a [30]) accompanying with lowering of activation energy with increasing Fe_2O_3 content (Figure 5b) [28, 30]. The conduction of the glasses, n-type semiconducting, of these systems [27-29] confirmed SPH in the non-adiabatic regime in common. This non-adiabatic nature is probably due to smaller content of Fe_2O_3 than those in vanadium tellurite glasses. The maximum Fe_2O_3

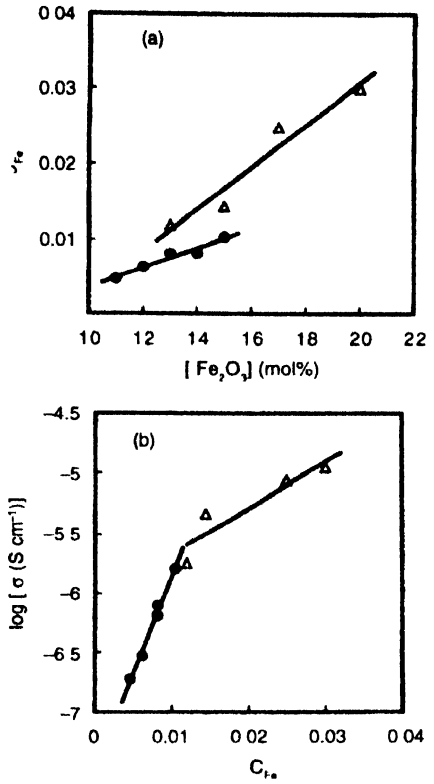

Figure 4. Effects of C_{Fe} on dc conductivity at T = 473K for Fe_2O_3-Sb_2O_3-TeO_2 [28] and Fe_2O_3-SrO-TeO_2 [29] glasses For (a) and (b), ● : Fe_2O_3-Sb_2O_3-TeO_2 glasses ; Δ : Fe_2O_3-SrO-TeO_2 glasses. (a) C_{Fe} *vs* Fe_2O_3 content [30], (b) Conductivity *vs* C_{Fe} [30]

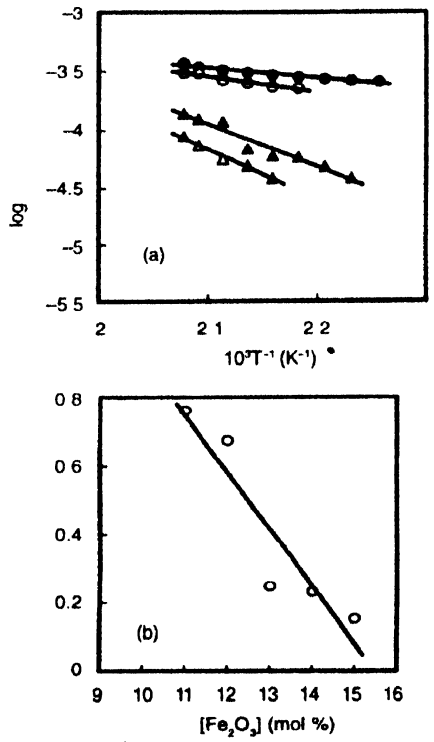

Figure 5. Temperature dependence of dc conductivity for Fe_2O_3-Sb_2O_3-TeO_2 glasses [28] [30]. (a) Conductivity vs. temperature [28] [30]. ● : 14 Fe_2O_3–1.5 Sb_2O_3–84.5TeO_2, o : 13Fe_2O_3–1.5Sb_2O_3–85.5TeO_2, ▲: 12Fe_2O_3–1.5Sb_2O_3 – 86.5TeO_2, Δ : 11Fe_2O_3 – 1.5Sb_2O_3 – 87.5TeO_2(mol%). (b) Activation energy W vs. Fe_2O_3 content [30].

content in these glass formation regions is commonly 15–23 mol% [9, 27-29]. This makes the occurrence of adiabatic hopping difficult because of large Fe–O–Fe spacing due to these low Fe_2O_3 concentrations. The linear conductivity-temperature relationships gave single-valued activation energies for Fe_2O_3–Sb_2O_3–TeO_2 [28] and Fe_2O_3–SrO–TeO_2 [29] glasses similar to iron silicate [19] and phosphate [31] glasses. The SPH transport was valid to low temperatures, but no variable range hopping was observed for binary [32] and ternary [27-29] iron tellurite glasses. This is, as stated, due to the low concentration of Fe_2O_3 (less than 23 mol%) in these glasses, causing large Fe-O-Fe spacing and low $N(E_F)$.

3.2 Multiphonon tunneling conduction :

Shimakawa [33], assuming microclusters in a glass network, revealed that the dc and ac conductivities of V_2O_5–P_2O_5 [1] and V_2O_5–TeO_2 [10] glasses could also be interpreted by multiphonon tunneling of large polarons between microclusters in the glass. The conductivity due to this model is predicted by [33],

$$\sigma = \sigma_0 T^n, \tag{5}$$

where σ_0 is a constant depending on glass composition and n is nonintegral number. The microcluster was an assumption. Recently, 20 to 40 nm size microcrystalline grains were observed in V_2O_5–CoO–TeO_2 glasses [34] by TEM, and the dc conduction of these glasses could be well explained by this multiphonon tunneling transport model [33] for a wide temperature range (330–475K). At temperatures higher than $\Theta_D / 2$, the conduction was due to normal SPH, but for $T<\Theta_D / 2$ deviation from the relation $\log(\sigma T) - T^{-1}$ in intermediate temperature range could not be explained by the Greaves' [3] and Mott's [20] VRH models, respectively. As Figure 6 shows, the Shimakawa model [33] [eq. (5)] fits well to the conductivity data in a wide temperature range. Thus, this model has adaptability to other semiconducting glasses containing semiconducting micro or nanocrystals (nanocomposite glasses).

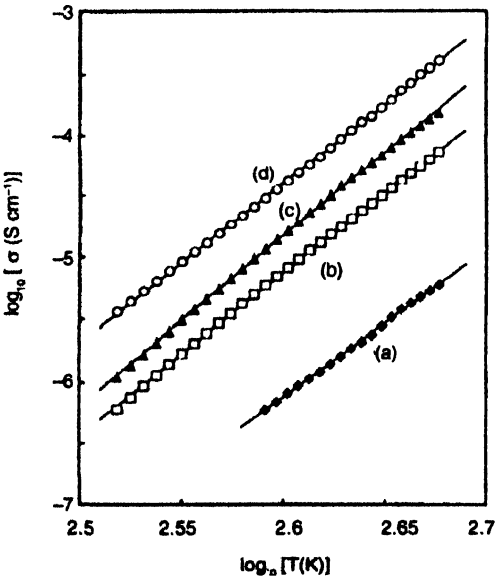

Figure 6. log σ vs. log T for xV_2O_5–10CoO–(90–x)TeO_2 (mol%) glasses [34]. (a) x = 40, (b) x = 50, (c) x = 60, (d) x = 70.

4. Thermoelctric power

The Seebeck coefficient (Q) was investigated for vanadium tellurite glasses [35]. The results, similar to those for V_2O_5–Bi_2O_3 glasses [36], indicated almost unchanged Q values for high temperatures and obeyed the Heikes formula [37]

$$Q = (k/e)[\ln\{C(1-C)\} + \alpha'], \tag{6}$$

where C is fraction of reduced metal ion to total transition metal ion, α' is a constant of proportionality between the heat transfer and the kinetic energy of an electron. For $\alpha' < 1$ [38], conduction is due to SPH, but for $\alpha' > 2$ [8], conduction is caused by large polaron. As Figure 7 shows, almost temperature invariant Q values for V_2O_5–Sb_2O_3–TeO_2 and V_2O_5–Bi_2O_3–TeO_2 glasses [35] obey eq. (6), indicating that the transport of these glasses was small polaronic. V_2O_5–RO–TeO_2 glasses containing the second transition metal oxide (R=Mn [26] or Ni [39]), presented temperature invariant Q values apparently expressed by eq. (6). However, extension of the Heikes formula [eq. (6)] for glasses containing two transition metal ions between different transition metal ions is necessary for more detailed analysis. Finally, it is noted that these vanadium and iron tellurite glasses are stable in air, this enables further studies of these glasses for application.

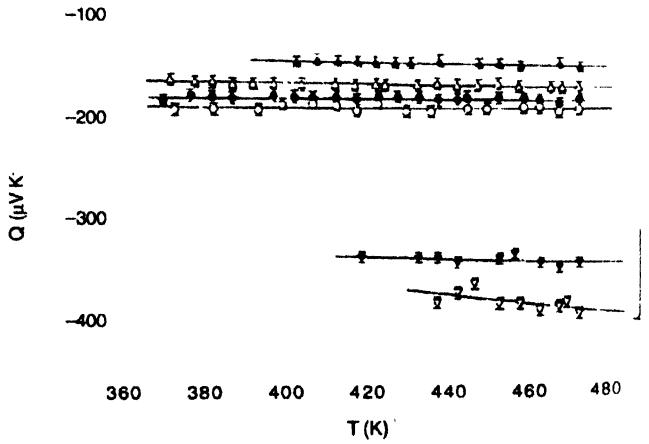

Figure 7. Seebeck coefficient Q of V_2O_5–Sb_2O_3–TeO_2 and V_2O_5–Bi_2O_3–TeO_2 glasses [35]. (○, ●, Δ) : xV_2O_5–$4Sb_2O_3$–(96-x)TeO_2 (mol%) glasses. ▲ : $26V_2O_5$–$3Sb_2O_3$–$71TeO_2$ (mol%) glass. ○ : x = 62. ● : x = 56. Δ : x = 44; (▽,▼) : xV_2O_5–$6Bi_2O_3$–(94-x)TeO_2 (mol%) glasses. ▽ : x = 69. ▼ : x = 60.

5. Applications

5.1. Effect of pressure on conductivity :

When a high pressure is applied to semiconducting tellurite glasses, hopping transport is expected to increase, because the mean spacing between transition metal ions becomes shorter than that before applying pressure. If this effect is large and reversible, some glasses may be applicable to a pressure sensor.

The ultrahigh pressure effects on density and refractive index of silica glass has been reported [40-42] and an irreversible change of the properties beyond a threshold pressure took place. Murawski and Gzowski [31] reported pressure dependence of conductivity for Fe_2O_3–P_2O_5 glasses with no threshold pressure. Recent report indicated that the dc conductivity of V_2O_5–PbO–TeO_2 glasses [43] reversibly increased (Figure 8a) or decreased (Figure 8b) on applying or releasing pressure (0-6GPa). These change were more remarkable in bulk glass sample than in powder glass sample. Although the conductivity change was low (a factor of 2-4) because of somewhat rigid in glass structure, the experiments provided a possibility of new research, *i.e.*, the hopping transport in compact glasses.

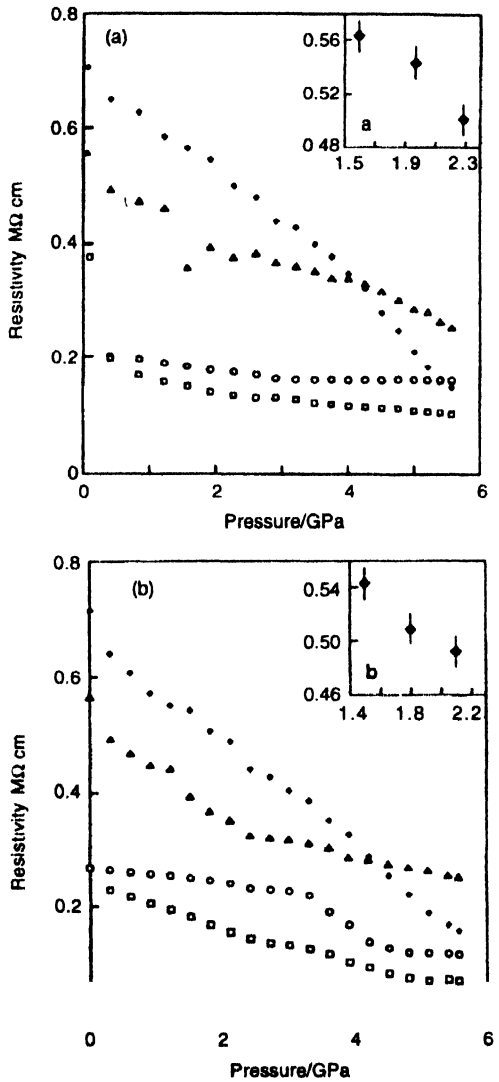

Figure 8. Effect of pressure on resistivity of xV_2O_5–20PbO–(80-x) TeO_2 (mol%) glasses [43]. (a) on increasing pressure, Δ : x = 60, powder, o : x = 40, powder ; □ : x = 50, powder, ◆ : x = 50, bulk sample. (b) on decreasing pressure, Δ : x = 60, powder, o : x = 40, powder, □ : x = 50, powder, ◆ : x = 50, bulk sample.

5.2. *Effect of atmospheric gas on conductivity :*

Gas – sensing properties of semiconducting ceramics at high temperatures have been well known, and attempts for developing gas-sensing materials and sensor devices have been extensively performed. In gas-sensing of conducting ceramics, *e.g.*, SnO_2 or ZnO, absorption and desorption of reducing or oxidizing gas on ceramics surface are basic phenomena, which modulates concentration of electron in band conduction. However, no attempts were made on the feasibility of gas-sensing for vanadate or iron tellurite glasses in small polaronic conduction.

A gas-sensing experiment was made for V_2O_5–SrO–Sb_2O_3 glasses [44] using a pressed-glass powder pellet which was then sintered at temperatures lower than the glass transition temperature (Tg), thus a porous glass pellet sample was obtained. When atmospheric gases, O_2 and Ar, were exchanged each other at temperatures 160–220°C for the sample, reversible changes in the dc conductivity were observed (Figure 9), though conductivity response in exchanging gases was low [44]. The gas sensitivity for oxygen was obtained to be 4.5. The gas-sensing mechanism of these glasses could be well explained by a gas (O_2) diffusion and desorption model [44], which gave a $t^{1/2}$ proportional conductivity response on introducing O_2 gas (t : time after gas introduction).

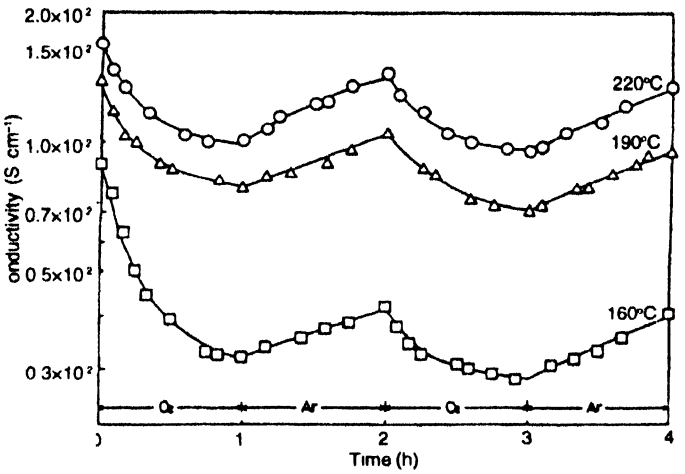

Figure 9. Changes in conductivity of $73V_2O_5$–18SrO–$9Sb_2O_3$ (mol%) glass with time at different temperatures on alternate switching of O_2 and Ar gases [44].

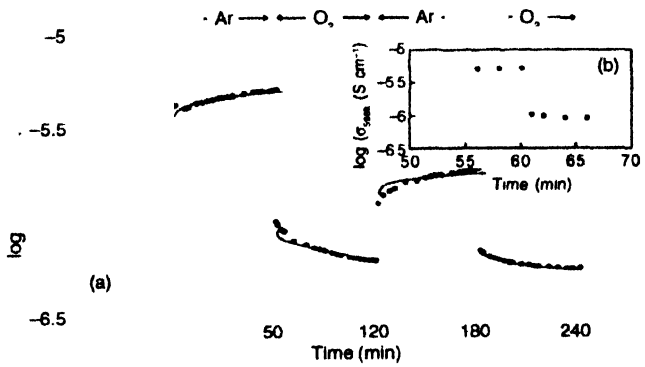

Figure 10. (a) Changes in dc conductivity of $15Fe_2O_3$–5Sb–80TeO_2 (mol%) glass with time at 598 K on alternate switching of Ar and O_2 gases [47]. The solid lines are calculated using eqs. obtained from gas diffusion model in Ref. [47]. (b) Changes in conductivity of $15Fe_2O_3$–5Sb–80TeO_2 (mol%) glass between 55 and 58 min at T = 598K, showing the sudden change in conductivity from 60 to 61 min [47].

These O_2 gas-sensing behaviour was also observed for n-type semiconducting V_2O_5–Sb_2O_3–TeO_2 [45] and V_2O_5–SnO–TeO_2 [46] glasses. The results were understood by a gas diffusion model, similar gas-sensing mechanism [44]. In particular, Fe_2O_3–Sb–TeO_2 glasses [47] showed a high sensitivity on alternate switching of Ar and O_2 gases (Figure 10) because, in addition to the gas diffusion, abrupt changes in conductivity due to chemisorption occurred at the sample surface. Thus the glasses gave a large gas-sensitivity of 8.1 at 325°C.

These above results suggest that if glass structure is optimized for easy diffusion and rediffusion of gases for sensing, these semiconducting glasses have the potential applicability to a gas sensor.

6. Conclusions

DC conduction properties of semiconducting vanadium and iron tellurite glasses and the feasibility of their applications were reviewed. The conduction of ternary vanadium tellurite glasses were due to small polaron hopping in the adiabatic or non-adiabatic regime. Variable-range hopping transport took place depending on glass composition. For glasses containing nanocrystallites, like the V_2O_5–CoO–TeO_2 system, the Shimakawa's multiphonon-tunneling model could explain the conductivity.

Ternary iron tellurite glasses exhibited relatively high conductivity with about 20mol% iron oxide, and presented non-adiabatic small polaron hopping conduction. The variable-range hopping transport was not yet observed. Increase in Fe_2O_3 content increases fraction of Fe^{2+} concentration to Fe total ion concentration and decreases activation energy, causing effective increase in conductivity.

The glasses (of both glass forming systems) increased their conductivity on applying pressure, and provided gas-sensing behaviour at elevated temperatures due to gas diffusion into and rediffusion from the glass. Further investigations are expected on their applications.

References

[1] M Sayer and A Mansingh *Phys. Rev.* **B6** 4629 (1972)

[2] G S Linsley, A E Owen and F M Hayatee *J. Non-Cryst. Solids* **4** 208 (1970)

[3] G N Grieves *J. Non-Cryst. Solids* **11** 427 (1973)

[4] H Hirashima, D Arai and T Yoshida *J. Am. Ceram. Soc.* **68** 486 (1985)

[5] A K Bandyopadhyay, J O Isard and S Parke *J. Phys.* **D11** 2559 (1978)

[6] L Murawski *J. Mater. Sci.* **17** 2155 (1982)

[7] M Sayer and A Mansingh *J. Non-Cryst. Solids* **58** 91 (1983)

[8] I G Austin and N F Mott *Adv. Phys.* **18** 41 (1969)

[9] V Kozhukharov, R Marinov and G Grigorova *J. Non-Cryst. Solids* **28** 429 (1978)

[10] V K Dhawan, A Mansingh and M Sayer *J. Non-Cryst. Solids* **51** 82 (1987)

[11] E GatteF and Y Dimitriev *Phil. Mag* **B40** 233 (1979)

[12] H Hirashima, Y Watanabe and T Yoshida *J. Non-Cryst. Solids* **95** 327 (1986)

[13] N Mochida, K Takahashi, K Nakada and S Shibusawa *J. Ceram. Assoc. Jpn.* (Yogyo-Kyokai-Shi) **86** 317 (1978)

[14] N Mochida, K Takahashi and S Shibusawa *ibid.* **88** 583 (1990)

[15] H Hirashima and T Tanaka *ibid.* **97** 1150 (1989)

[16] T Naito, T Namekawa, A Kato and K Maeda *J. Ceram Soc. Jpn* **100** 685 (1992)

[17] F R Landsberger and P J Bray *J. Chem. Phys.* **53** 2257 (1970)

[18] R Iordanova, Y Dimitriev, V Dimitrov and D Klissurski *J. Non Cryst. Solids* **167** 74 (1994)

[19] R A Anderson and R K MacCrone *J. Non-Cryst. Solids* **14** 112 (1974)

[20] N F Mott *Phil. Mag.* **19** 835 (1969)

[21] H Mori, T Kitami and H Sakata *J. Non-Cryst. Solids* **168** 15 (1994)

[22] H Mori, J Igarashi and H Sakata *Glastech Ber Glass Sci Technology* **68** 327 (1995)

[23] H Mori, K Gotoh and H Sakata *J Non-Cryst Solids* **183** 12 (1995)

[24] S Mandal and A Ghosh *Phys Rev* **B49**, 3131 (1994)

[25] H Hirashima and T Kawaguchi *J. Ceram. Soc Jpn* **97** 114 (1989)

[26] K Sega, Y Kuroda and H Sakata *J Mater Sci.* **33** 1303 (1998)

[27] H H Qiu, M Kudo and H Sakata *Mater Chem Phys* **51** 25 (1997)

[28] H H Qiu, H Mori, H Sakata and T Hirayama *J Ceram Soc Jpn* **103** 32 (1995)

[29] H H Qiu, H Sakata and T Hirayama *J Chin Ceram Soc* **24** 58 (1996)

[30] H H Qiu, Ph D Thesis (1999) (Tokai University, Japan)

[31] L Murawski and O Gzowski *Acta Phys Polon* **A50** 463 (1976)

[32] H Binczycka, O Gzowski, L Murawski and J Sawicki *Phys Sta. Sol* (a) **70** 51 (1982)

[33] K Shimakawa *Phil. Mag* **B60** 377 (1989)

[34] H Sakata, K Sega and B K Chaudhuri *Phys. Rev.* **B60** 3230 (1999)

[35] H Mori and H Sakata *J. Mater. Sci.* **31** 1621 (1996)

[36] A Ghosh *J Appl Phys* **65** 227 (1989)

[37] R R Heikes *Thermoelectricity*, (ed) R R Heikes and R W Ure (New York · Interscience) p81 (1961)

[38] N F Mott *J. Non-Cryst. Solids* **1** 1 (1968)

[39] K Sega, H Kasai and H Sakata *Mater. Chem. Phys.* **53** 28 (1998)

[40] P W Bridgman and I Simon *J. Appl. Phys.* **24** 405 (1953)

[41] H M Cohen and R Roy *J. Am. Ceram. Soc* **44** 523 (1961)

[42] H M Cohen and R Roy *ibid* **45** 398 (1962)

[43] H Sakata, M Amano and T Yagi *J. Non-Cryst. Solids* **194** 198 (1996)

[44] H Sakata, M. Amano, Y Kawashima and T Okamoto *J Ceram Soc. Jpn.* **102** 317 (1994)

[45] H Mori and H Sakata *Mater. Chem. Phys.* **45** 211 (1996)

[46] H Mori and H Sakata *J. Mater. Sci.* **32** 5243 (1997)

[47] S Chakraborty, H Satou and H Sakata *J. Appl. Phys.* **82** 5520 (1997)